

Self-Diffusion in Mesoporous Solids at Sub- and Supercritical Conditions

*Philipp Zeigermann**, *Muslim Dvoyashkin**, *Roger Gläser[†]* and *Rustem Valiullin**

*Fakultät für Physik und Geowissenschaften, Universität Leipzig, Leipzig, Germany

[†]Institut für Technische Chemie, Universität Leipzig, Leipzig, Germany

Nowadays heterogeneous catalysis is a commonly used process in chemical synthesis. Here, micro- and mesoporous solids, acting as supports with high surface area, are of utmost importance. Often high pressure environments are required to ensure efficient mass transport of the educts to the catalytic active sites and removal of the products. Because of their superior dynamical properties (low viscosity, no surface tension and high diffusivity) and the high tunability of these properties the supercritical state is here of particular interest. The benefits of using supercritical solvents in chemical synthesis are well documented in the literature [1,2].

Recently it was demonstrated that pulsed field gradient nuclear magnetic resonance (PFG NMR) provides a complementary tool to probe phase state and, in particular, transport properties of near-critical fluids confined to mesoporous systems [3]. In this work, the intra-porous diffusivities at sub- and supercritical conditions along an isochore have been probed and a shift in the intra-porous critical temperature to lower values has been observed. To gain further understanding, a complete phase diagram and its interrelation with the transport properties are of particular importance.

Here, we present an experimental scheme designed to probe self-diffusion of intraporous fluids with PFG NMR under high pressure conditions. Particularly, in the presented setup the thermodynamic conditions may be varied in an isothermal, isobaric or isochoric way. Thus, it allows the exploration of the whole near-critical phase space of different supercritical solvents or mixtures.

As an example, we will present results on the self-diffusion coefficient of sub- and supercritical ethane in mesoporous silicon (Fig.1) [4]. In this way we have assessed the phase-state of bulk and intra-porous ethane and have demonstrated the tunability of transport properties by using supercritical solvents at slightly different pressures. In addition we compare the behaviour of bulk diffusivities with intra-porous self-diffusion and show that diffusivities may be tuned by changing pressure in bulk supercritical fluids but this is not necessarily the case for the intraporous fluids.

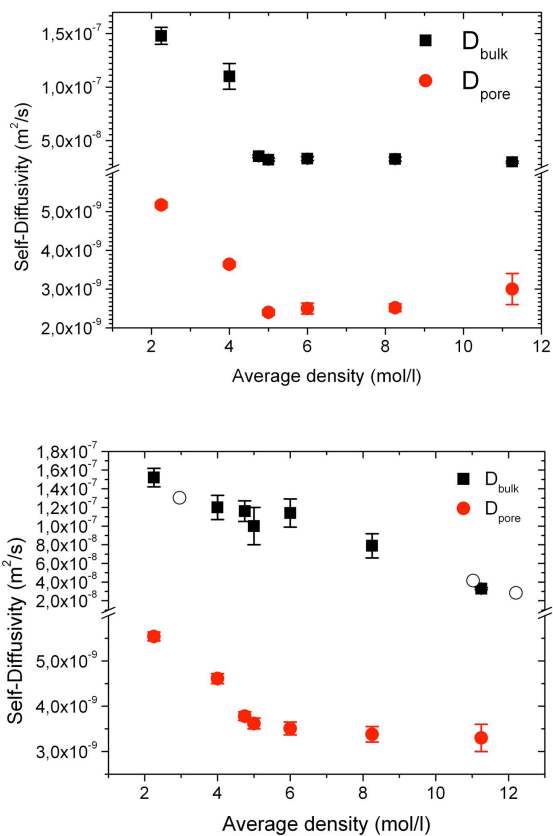


Fig.1 Self-diffusivity of ethane in bulk (squares) and in mesoporous silicon (circles) under sub-(top) and supercritical (bottom) conditions.

References

- [1] A. Baiker, Chem. Rev. 99, 453–473 (1999).
- [2] A. I. Cooper, Adv. Mater. 15, 1049–1059 (2003).
- [3] M. Dvoyashkin, R. Valiullin, J. Kärger, W.-D. Einicke, and R. Gläser, Journal of the American Chemical Society 129, 10344–10345 (2007).
- [4] P. Zeigermann, M. Dvoyashkin, R. Gläser and R. Valiullin, AIP Proceedings of MRPM10 (2010).